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Gasification and reforming of biomass and waste samples by means of a novel catalyst

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Abstract

This study conducted gasification and catalytic reforming experiments with the expectation of obtaining new advantages on energy recovery and aimed for the development of an effective catalyst. Initially, the use of thermal gasification technology for waste treatment in line with waste-to-energy strategies was reviewed. Technological systems which have gasification were classified and their current status was discussed. Then, the results of gasification and reforming experiments showed that product gas with 50% H_2 or more was obtained by using a Ni catalyst on a mesoporous silica–based SBA-15 support (NiO/SBA-15), which we newly developed. Experiments using wood feedstock revealed that H_2 production by the catalyst was better when the NiO content was 20% (W/W) or more than when another catalyst or the Ni catalyst with a lower Ni loading was used. Tar formation as a by-product was also well controlled by the catalyst, and use of a catalyst with 40% NiO reduced the tar concentration to less than 0.2 g/m^3_N. Experiments using a mixed feedstock of wood and RPF resulted in an increase in hydrocarbon concentration because of insufficient reforming. This finding suggests that future work is required to find a better solution to wood and RPF co-gasification.

Keywords: Gasification · Catalytic reforming · Hydrogen · Ni catalyst · Tar

Introduction

Thermal treatment of solid wastes, including municipal solid waste (MSW) and other biomass waste, has been the core technology for reducing waste volume for the purpose of sanitation. In the face of global warming, energy recovery by waste-to-energy (WtE) is a crucial issue in this field. It is also required to recover any materials from the disposal process of biomass wastes. Hence, gasification has now become a very attractive technological process for disposal and further utilization of waste biomass, because it has great potential in power generation and gas utilization. Thermal gasification using partial oxidation provides H_2, CO, and CO_2 as major components, and CH_4 and other hydrocarbons as minor components [1-3]. The gaseous mixture can be used as gas engine fuel and in fuel-cell applications after required treatments such as gas purification have been performed. Carbon monoxide can also be used as a raw material in chemical synthesis processes in the area of C1 chemistry [4].

Besides being useful for recovering gases for such uses, gasification plays an important role as a pre-treatment in the combustion of heterogeneous solid wastes. Here, we review the use of thermal gasification technology in waste treatment. Technologies that include gasification as the first step are classified here as shown in Fig. 1. The use of high-temperature combustion as the second process has become popular in the thermal treatment of MSW in Japan since the beginning of the 2000s. This is called the gasification and melting process, and today about one-tenth of Japan's 1,172 MSW incineration plants as of the 31st of March, 2014 are of this type [5]. The dioxin issue which emerged in the 1990s accelerated the introduction of these types of plant. However, the process is essentially based on high-temperature combustion and occasionally needs more energy to operate than conventional stoker incineration plants. In recent years, this high energy requirement seems to have caused stagnation in any increase in the use of gasification and melting in Japan. This stagnation has been exacerbated by the fact that: 1) the potential advantage of producing slag from gasification and melting processes has declined, because a drop in construction activity has reduced the value of this product in materials recycling; and 2) advanced flue gas technologies can now be used in all types of thermal treatment plants; gasification and melting plants therefore no longer offer great advantages.

Nevertheless, there are some gasification and reforming–type plants in Japan that are used for disposal and energy/materials recovery from MSW and industrial wastes [6]. A high-temperature (~1,300 ºC) partial oxidation process is usually used in the reforming process. This type of plant was introduced from Europe to Japan in the late 1990s, and several plants have been employed as new thermal treatment facilities for solid wastes including MSW [7]. The gas produced is used for power generation by gas engines, and the solids, such as slag and metal oxides, are also recovered. However, this type of plant has high running costs because of the need to supply pure oxygen and the need for advanced wastewater treatment. Therefore, in today's economic climate, the number of these plants is not increasing. Additionally, one of the disadvantages of the gasification process so far is low cold gas efficiency because of the high operating temperature.

Therefore,it is necessary to reduce the temperature and to decrease the activation energy of reactions by using a catalyst. The aims of catalyst use for gasification and reforming process are: 1) to increase H_2 and CO syngas recovery at lower temperatures, and 2) to reduce tar components to avoid negative influence to the use of syngas. Many studies have been published with regard to catalytic gasification and reforming processes for biomasses

including solid waste [8-12]. Various metals such as Ni have been examined in their performance for obtaining higher H_2 production from biomasses. However, the results of those studies did not indicate sufficient effect on the H_2 and CO recovery.

Figure 2 shows the process design concept which includes gasification, the catalytic reforming process and further possible gas conversion processes for gas utilizations of fuel and raw material. In this process, biomass waste is first gasified at 750 ºC, at which temperature H_2 gas is generated effectively [10], using steam and oxygen as gasification agents. The resulting gas is then reformed by reactions such as a shift reaction, through the action of a catalyst, to increase the H_2 and CO contents. Decomposition of tar constituents also occurs at this stage. The study covers this part of the process, as illustrated by the area circled by a dotted line in Fig. 2. Additionally, the reformed syngas can be converted by the reverse water-gas shift (RWGS) process from CO_2 to CO by means of a catalyst [13]. Another gas conversion selection is methanation, by which synthesized natural gas (SNG) can be obtained [14].

In the above processes, it is very important to obtain a high concentration of H_2 in the syngas.Therefore, we aimed to develop an effective catalyst to generate higher concentrations of H_2 from gasification and steam reforming at 750 ºC. The target H_2 concentration in the gas was set at more than 50% (V/V), without nitrogen, and the target yield of H_2 was set at 40 mol/kg-feedstock or more. Furthermore, tar formation is a serious problem in commercial plant operation. The levels and types of tar in syngas are substantially affected by the operating conditions used [15], and it is necessary to consider the composition of tar, including such compounds as phenolics and PAHs. Here, we expected the tar concentration reduction to be no more than 0.2 g/m^3_N after the reforming process.

Experimental

Materials

Feedstock

Two feedstock samples were used. One was waste wood from demolition residue, its main component being Japanese cedar, and the other was refuse paper and plastic fuel (RPF), in the form of commercial product samples The wood sample was crushed and sieved into 1- to 2-mm particles for the experiment. The RPF sample was also crushed; however, it was not in particle form but had a flocculent shape because it contained plastic materials. The results of proximate and ultimate analyses of the materials are shown in Table 1. There was a big difference (a factor of 20) in ash content between the wood and RPF samples; the value of the RPF was much higher than that of the wood. The heat value of RPF was also higher than that of wood, probably because of the plastic content of the former. The elemental H content of RPF was about 28% higher than that of wood, and the Cl and S contents of RPF were also higher than those of the wood. These results showed that the wood sample was clean, whereas the RPF potentially contained both combustibles and impurities.

Catalyst

Two kinds of catalysts were used in the experiment: a nickel (Ni) catalyst on silica base material and an alloy pipe catalyst, both of which were original developments. First, the mesoporous silica catalyst named SBA-15 was prepared using two synthesis methods [16,17]. In the direct synthesis method modified from an original

method [16], the block copolymer Pluronic P123 was mixed with H_2SO_4, $Ni(NO_3)_2 \bullet 6H_2O$, and tetraethyl orthosilicate at room temperature. The mixture was aged at 60 ºC until a white precipitate appeared and then immediately evaporated at 100 ºC overnight. The solid product was dried at 150 ºC for 5 h and then calcined at 500 ºC for 10 h then 800 ºC for 2 h. Next, in the post-synthesis method, SBA-15 was synthesized at 60 ºC according to the method by Lu et al. [17]. The SBA-15 was added to ethanol dissolved in $Ni(NO_3)_2 \bullet 6H_2O$ and dispersed for 6 h under supersonic. The mixture was then dried at room temperature and calcined at 400 ºC for 5 h. The solid products were characterized by using X-ray diffraction (XRD), nitrogen adsorption isotherm measurement, and transmission electron microscope (TEM) observation. The nitrogen adsorption-desorption isotherms of NiO/SBA-15 were obtained using the two synthesis methods (Fig. 3). The isotherms were similar to IUPAC classification type IV, clearly indicating that these materials possessed mesoporous structures. A type-H1 hysteresis loop was observed regardless of the synthesis method. However, when direct synthesis was utilized, NiO particles were dispersed into the SiO_2 structure of SBA-15 and were not located in the SBA-15 pores, unlike the case with post-synthesis. The TEM images showed an ordered mesoporous structure typical of SBA-15, irrespective of the preparation method (Fig. 3 (a) and (b)) [13]. The images showed that, with direct synthesis, NiO particles were highly dispersed (monodispersed) in the SiO_2 structure of SBA-15. In contrast, with post-synthesis, aggregates of NiO particles were observed. In further experiments we investigated other metal elements, namely copper (Cu) as CuO, cobalt (Co) as CoO, cerium (Ce) as CeO_2, and rhodium (Rh) as Rh_2O_3. CuO and CoO were employed as alternatives to Ni, and CeO_2 and Rh_2O_3 were used as bimetal compounds with Ni.

Hastelloy and Kovar alloy pipe catalysts, which included such components as Ni, Cr, Mo, Fe, and Co, were also used. These catalysts have been developed as cost-effective alternatives to the usual Ni catalyst [18]. In commercial applications the pipe structure was expected to be easily applicable to flue-gas reactions.

Additionally, CaO reagent was applied in every run to the top surface of the catalyst layer in the reactor to improve the catalytic performance and help prevent coke deposition during the catalytic reactions.

Apparatus

A bench-scale gasification unit was equiped for the gasification and catalytic reforming experiment, and the schematic representation is shown in Fig. 4. The apparatus consists mainly of two tubular reactors: the primary reactor-gasifier and the secondary reactor-reformer. Both reactors are made of stainless steel and have 35-100 mm ID and 1,210-1,620 mm H as shown in the figure. Both reactors were heated and controlled at 750 ºC from outside by electric mantle heaters and operated at atmospheric pressure. The gasifier has a double tubular structure for introducing solid particles from the feeder into the reactor. The reactor was operated in updraft mode and the arranged solid sample was fed to the gasifier at a rate of approximately 60 g/h by a quantitative delivery device. All of the pipelines were maintained at above 300 ºC by heaters to avoid the condensation of tar components. After the reactors had been preheated to 750 ºC and held there for 1-2 hours, the feed stocks were sequentially supplied into the gasifier. Steam and oxygen were also supplied when necessary from the bottom of the gasifier.

Experimental conditions

Gasification and reforming experiments were conducted on the recovery of hydrogen from combustible samples with a focus on the effects of the catalyst we developed. There were two basic operational parameters in the gasification process: the amount of steam injected, namely the ratio of steam to carbon in the feedstock, or S/C (mol/mol) ratio; and the equivalent ratio (ER), which was defined as the ratio of the actual oxygen amount to the amount required for complete combustion. As standard conditions in this study, we set S/C as 1.5 and ER as 0.2. Experimental runs were designed to evaluate catalyst performance, and the type and composition of the effective Ni element of the catalyst were varied.

Measurements

Gas sampling and measurement were conducted before and after gas entry to the reformer as shown in Fig. 4. The sample gases were introduced into connected impingers set in ice baths. After tar sampling and removal, inorganic gases including H_2, CO and CO_2 and some gaseous organic compounds including CH_4 and hydrocarbons were quantified semi-continuously, at 2-3 minutes intervals, by using inline gas chromatographs (MicroGC 3000; Agilent Technologies Japan, Ltd.) with a TCD (thermal conductivity detector). The hydrocarbons include aliphatic compounds such as C_2H_4 and aromatic ones such as benzene. Gas concentrations measured in short intervals varied due to fluctuations in the feeding rate of the solid sample, and an average number was calculated using the data obtained in 1 hour after the experiment system reached a steady state.

Tar measurement was conducted in three ways; gravimetric measurement, PAH and phenolic compound determinations. A detailed description of the measurement methods is given elsewhere [15].

Results and discussion

Gasification and reforming for syngas production

Forty runs were conducted in the gasification and reforming experiments; Table 2 shows representative data from half of these runs. Gas compositions are shown as nitrogen-free calculations. Initially, for wood samples, the H_2 concentration in the gasified gas was below 36% (V/V) and the representative values were in the range of 20% to 30%. Both CO and CO_2 concentration were about 30%, and the data were susceptible to variations in conditions such as feeding rate. CH_4 concentrations were in the range of 4% to 12%, and those of other hydrocarbons ranged from about 3 to 5 %. After the reforming, the H_2 concentration was increased by catalytic reactions such as the shift reaction. However, the concentration did not reach 40% without the catalyst or when the catalyst performance was very low (Runs 10, 14, and 15). The original Ni catalysts on SBA-15 (NiO/SBA-15) showed good performance with increasing H_2 concentrations and the maximum value was obtained in Run 7 (56.8 % (V/V)). In the experiments conducted using wood feedstock, the NiO/SBA-15 catalyst gave good results in both H_2 formation and hydrocarbon content reduction. Indeed, a difference in catalytic performance was recognizable in terms of CH_4 and CnHm reduction efficiency. The reduction values of CH_4 and CnHm were 13.6% and 25.0% respectively without catalyst, whereas those in the run using NiO/SBA-15 (NiO: 20%) were 91.8% and 90.1%, respectively. These findings suggested that tar decomposition reactions occurred during the reforming process. The heat value obtained from the reformed gas was about 5 MJ/m^3; these gases can be used for power generation by using gas engines.

Experiments that used metal elements other than Ni from Runs 10 to 13 did not result in good performance in

terms of H_2 recovery or CH_4 and hydrocarbon concentration reductions. Nickel catalysts have been used for reforming in many industries, and they also gave good results here. Rhodium is known to be a powerful oxidative catalyst, and our results for CH_4 and hydrocarbon reduction supported this performance to a small degree. Further investigations may be needed to quantify the catalytic performance of rhodium in biomass gasification applications.

Hastelloy alloy was tested under several conditions. However, none of the experimental runs yielded good performance in terms of H_2 formation (see Runs 14 and 15). Tagawa et al. [18] applied this alloy pipe material to reforming the alkane tetradecane as a model tar compound in the context of the development plan in Fig. 2; they reported higher performance in tested alloy samples than this study. However, the material did not give good results. This was probably because the alloy pipe did not have sufficient specific surface area or reaction sites in the heterogeneous field of biomass gasification. Our experiments showed a possibility for improving performance by adding NiO and CeO_2.

The chemical space in CaO allows hydrocarbons and steam to readily become attached to the catalyst surface; this increases their opportunity to react with each other, thus promoting the reforming reaction.

Effect of NiO content of catalyst to gas recovery

The effects of the catalyst of NiO/SBA-15 on gas composition and hydrogen yield are shown in Fig. 5. In the figure, over 40% (V/V) H_2 was obtained with NiO present on the SBA-15 medium regardless of proportion, compared to yield without a catalyst. Among the experiments employing a catalyst, the H_2 concentration increased when the NiO content increased from 10% (W/W) to 40%, with a gentle slope. Increase in CO and decrease in CO_2 were siginificantly apparent at 10%, 20%, and 30% NiO, probably because of the RWGS reaction. H_2 yield was greater with an NiO content of 20% than of 10% or with no catalyst. The effect of NiO content on H_2 recovery did not greatly increase beyond 20 wt%. Considering the facts and the potential cost of catalyst application, it would be better to adjust the NiO content of the NiO/SBA-15 to 20%.

We did not investigate the effect of temperature on the composition of the gas generated. However, other studies [19,20] using the same apparatus have examined the effects of operational conditions (residence time, ER, S/C ratio, and gasification temperature) on the characteristics of the product gas. The results have indicated that appropriate steam and oxygen supplies were favorable for H_2 production, and that higher H_2 yields and heat values of the product gas can be achieved under sufficient residence times, high gasification and reforming temperatures. Increasing the S/C ratio has effectively enhanced the proportion of H_2 in the product gas. The presence of oxygen (ER from 0 to 0.3) can increase both H_2 yields and CO production efficiency [20].

Tar pollutant formation and removal

To apply the gasification process to commercial environmental plants for biomass waste disposal, it is very important to control tar formation so as to prevent problems caused by tar condensation. Table 3 shows tar measurement data obtained in the experiment. Tar was quantified in three different ways, as described in the Experimental section. For wood samples, the tar concentration determined by gravimetric measurement was in the range of 3 to 20 g/m^3_N, with an average of 11 g/m^3_N. The data varied widely owing to the variation in solid-sample feeding. The overall concentration of PAHs and phenols was in the range of 500 to 4200 mg/m^3_N

(average 2150 mg/m^3_N). PAHs and phenols made up about 20% of the gravimetric value, suggesting that unknown components remained in the tar matrix.

The graph in Fig. 6 is based on data on tar formation and removal during the processing of wood samples. The tar concentration in the reformed gases, as determined by using the gravimetric method, was roughly the same at NiO concentrations of 10 and 20% on SBA-15. It decreased to less than 0.4 g/m^3_N with an increase in the NiO content to 30 and 40%. We aimed for a tar concentration of 0.2 g/m^3_N (gravimetric value) after reforming. The results showed that an NiO content of 40% was needed for this purpose. However, Run 6 achieved 99.3% decomposition under these experimental conditions. Because the CaO material can decompose about 90% of gravimetric tar (as seen in Run 1 of Table 3) when no catalyst is used, the catalyst plays an important role in determining how completely the remaining 10% is decomposed. On the other hand, the effect of PAH and phenol concentration removal was apparent.

Gasification and reforming using RPF sample with wood

We were able to introduce a new concept that uses RPF as a mixture with wood materials, because both RPF and refuse-derived fuel (RDF) have been supplied and used as fuels in distribution systems for waste-derived fuels in Japan and other countries. In the experiment, RPF samples were mixed with the wood samples at 10% to 50% by weight. Figure 7 shows that the gas compostion and H_2 yield changes with the addition of RPF. An increase in the ratio of RPF to wood slightly decreased the H_2 and CO concentrations but raised the CO_2, CH_4, and hydrocarbon concentrations. This suggests that reforming became insufficient owing to an increase in hydrocarbon generation from plastic decomposition in RPF. It also suggests that the contact time between the gas and the catalyst layer needs to be lengthened in these circumstances. However, the H_2 yield was not reduced, but stayed at approximately 40 mol/kg-feedstock—the same as with wood material only. Gravimetric tar removal rates and PAH and phenol removal rates were lower than those for wood (Table 3). Therefore, future work is needed to obtain better results from wood and RPF co-gasification.

Conclusions

Thermal gasification and catalytic reforming experiments were conducted for the purpose of obtaining H_2 and CO as useful flammable gases. The aims were to develop an effective catalyst that would enable syngas production with 50% (V/V) H_2 or more and tar reduction to below 0.2 g/m^3_N in the gas. The results obtained were;

(1) A nickel catalyst on a mesoporous NiO/SBA-15 was found to be an effective catalyst for extracting H_2 and CO, and the maximum H_2 concentration reached was about 57% in syngas from wood samples.

(2) Experiments using wood feedstock revealed that H_2 production by the catalyst was better when the NiO content was 20% (W/W). It was appropriate to adjust the NiO content of the catalyst to 20% in light of this result and in consideration of catalyst cost.

(3) Tar formation was well controlled by the catalyst and the use of the catalyst with 40% NiO reduced the tar concentration to less than 0.2 g/m^3_N.

(4) The mixing of RPF to wood slightly decreased H_2 concentration but the yield was not reduced suggesting that reforming became inefficient. Future work is required to find a better solution to wood and RPF co-

gasification.

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Legends

Fig. 1 Technological systems in which gasification is a major process in the thermal treatment of solid wastes

Fig. 2 Gasification and catalytic reforming process of biomass waste in this study, and possible gas conversion process design

Fig. 3 Nitrogen adsorption–desorption isotherms and TEM images of 10wt%-NiO/SBA-15 obtained using the direct (a) and post-synthesis (b) methods as characterizations of meso-porous silica.

Fig. 4 Gasification and reforming experiment apparatus and gas sampling flow

Fig. 5 Effect of NiO content on gas composition and H_2 yield in catalytic reforming (Feedstock :Wood, Catalyst : NiO/SBA15, Temperature : 750 ºC, Because of the lack of necessary data, the H_2 yield at no catalyst is not plotted.)

Fig. 6 Gravimetric tar, PAHs and phenols in reformed gases and removal efficiencies by NiO contents (Feedstock:Wood, Catalyst : NiO/SBA15, Temperature : 750 ºC)

Fig.7 Gas composition and H_2 yield change with mixing RPF to wood sample (Catalyst: 20wt%-NiO/SBA-15, Temperature : 750 ºC)

Table 1 Proximate and ultimate analyses of the raw materials used

Analysis item	Wood sample	RPF sample
Proximate analysis		
Moisture (%)	11.4	3.9
Volatile (wt% dry)	84.0	83.6
Fixed carbon (wt% dry)	15.7	8.4
Ash ((wt% dry)	0.3	8.0
High heat value (MJ/kg dry)	19.8	24.0
Low heat value (MJ/kg dry)	16.0	21.2
Ultimate analysis		
C (wt% dry)	48.5	50.6
H (wt% dry)	6.3	8.1
O (wt% dry)	44.9	33.0
N (wt% dry)	<0.01	0.3
Cl (mg/kg dry)	46	400
S (mg/kg dry)	63	500

Table 2 Measurement data of inorganic gases and some aliphatic hydrocarbons

Run No.	Catalyst*	Feedstock sample	After gasification					After reforming					CH_4 reduction ratio (%)	CnHm reduction ratio (%)	Notes
			H_2	CO	CO_2	CH_4	CnHm	H_2	CO	CO_2	CH_4	CnHm			
1	No catalyst	Wood	28.0	22.0	39.0	6.6	4.4	37.0	16.0	38.0	5.7	3.3	13.6	25.0	
2	NiO/SBA15 (NiO:10%)	Wood	36.0	13.0	43.0	4.5	3.5	44.0	9.7	40.0	4.4	1.9	2.2	45.7	
3	NiO/SBA15 (NiO:20%)	Wood	23.4	31.5	31.6	9.2	4.3	50.4	23.3	25.2	0.75	0.42	91.8	90.1	
4	NiO/SBA15 (NiO:20%)	Wood	18.0	38.0	30.0	9.9	4.2	50.0	22.0	27.0	0.11	0.42	98.9	90.0	
5	NiO/SBA15 (NiO:30%)	Wood	21.3	35.9	27.0	10.5	5.3	53.1	26.0	20.5	0.00	0.43	100	92.0	
6	NiO/SBA15 (NiO:40%)	Wood	20.9	36.7	25.5	11.3	5.5	54.1	23.7	21.1	0.71	0.44	93.7	92.0	
7	NiO/SBA15 (NiO:20%)	Wood	26.1	38.2	19.7	11.5	4.5	56.8	20.4	21.3	1.00	0.51	91.2	88.7	ER:0.05
8	NiO/SBA15 (NiO:20%)	Wood	24.5	28.2	34.2	9.0	4.1	53.7	12.2	32.9	0.88	0.33	90.2	91.8	S/C:3.0
9	NiO/SBA15 (NiO:20%)	Wood	22.4	30.0	34.6	9.4	3.5	48.2	25.3	26.1	0.00	0.41	100	88.4	Catalyst:100g, CaO:100g
10	CuO/SBA15 (Cu:20%)	Wood	20.0	37.8	27.8	9.81	4.49	35.8	23.2	29.4	8.44	3.21	14.0	28.6	
11	CoO/SBA15 (Co:20%)	Wood	20.3	30.7	35.3	9.6	4.1	43.2	16.7	32.6	5.9	1.72	39.0	58.2	
12	Rh_2O_3/NiO/SBA15 (Rh:3%)	Wood	17.5	39.7	26.4	11.8	4.6	46.4	25.0	23.4	4.6	0.49	60.7	89.3	
13	Rh_2O_3/NiO/SBA15 (Rh:6%)	Wood	20.4	37.7	26.7	10.9	4.28	47.9	25.6	23.6	2.50	0.42	77.0	90.2	
14	Hastelloy® alloy	Wood	18.5	39.3	26.9	11.0	4.43	35.2	17.4	35.1	8.54	3.71	22.1	16.4	Alloy:250g, CaO:150g
15	Hastelloy® alloy/NiO CeO_2(NiO:5%)	Wood	31.0	15.0	45.0	4.8	4.6	39.0	10.0	47.0	2.1	1.9	56.7	58.4	
16	NiO/SBA15 (NiO:20%)	RPF(10%)/ Wood	16.9	37.3	28.1	12.2	5.6	49.5	24.2	22.8	2.90	0.59	76.2	89.3	
17	NiO/SBA15 (NiO:20%)	RPF(25%)/ Wood	15.7	33.6	29.8	13.0	8.0	46.8	23.5	24.8	3.88	1.04	70.1	86.9	
18	NiO/SBA15 (NiO:20%)	RPF(50%)/ Wood	14.3	32.8	28.7	13.8	10.4	47.3	19.3	27.2	4.58	1.67	66.8	83.9	
19	NiO/SBA15 (NiO:40%)	RPF(50%)/ Wood	13.3	34.0	30.1	11.8	10.8	51.5	19.3	24.3	3.18	1.69	73.2	84.3	
20	NiO/SBA15 (NiO:20%)	RPF(50%)/ Wood	12.0	34.0	30.0	12.0	12.0	51.0	28.0	22.0	0.79	0.26	93.2	97.8	Catalyst:100g, CaO:100g

* The amount of catalyst packed was usually 50g and 150g of CaO was employed. Different conditions were employed in some cases as shown in the notes.

Table 3 Tar and sulfur compound data and removal

Run No.	After gasification		After reforming		G-tar removal ratio (%)	PAHs+Phenols removal ratio (%)
	G-tar* (g/m^3_N)	PAHs+Phenols (mg/m^3_N)	G-tar* (g/m^3_N)	PAHs+Phenols (mg/m^3_N)		
1	8.4	1600	0.80	676	90.4	57.8
2	5.2	785	0.68	26.5	86.8	96.6
3	11	1230	0.55	21.0	95.0	98.3
4	10	2760	0.16	19.6	98.5	99.3
5	14	1360	0.37	20.3	97.4	98.5
6	18	4160	0.13	54.1	99.3	98.7
7	8.8	2450	0.19	29.3	97.8	98.8
8	6.3	3850	0.14	259	97.7	93.3
9	13	2100	0.66	12.4	94.9	99.4
10	18	2980	0.81	771	95.6	74.1
11	8.9	1060	0.39	115	95.7	89.2
12	20	3140	0.42	40.9	97.9	98.7
13	12	2330	0.31	17.6	97.4	99.2
14	10	1920	0.53	597	94.8	68.8
15	3.1	494	0.25	10.8	91.8	97.8
16	16	2210	0.51	13.6	96.7	99.4
17	6.4	1090	0.33	175	94.9	83.9
18	14	1350	0.73	181	94.9	86.6
18	8.0	2270	0.16	86.2	98.0	96.2
19	6.4	1090	0.33	175	94.9	83.9
20	12	2010	0.17	59.7	98.6	97.0

* Gravimetrically determined value

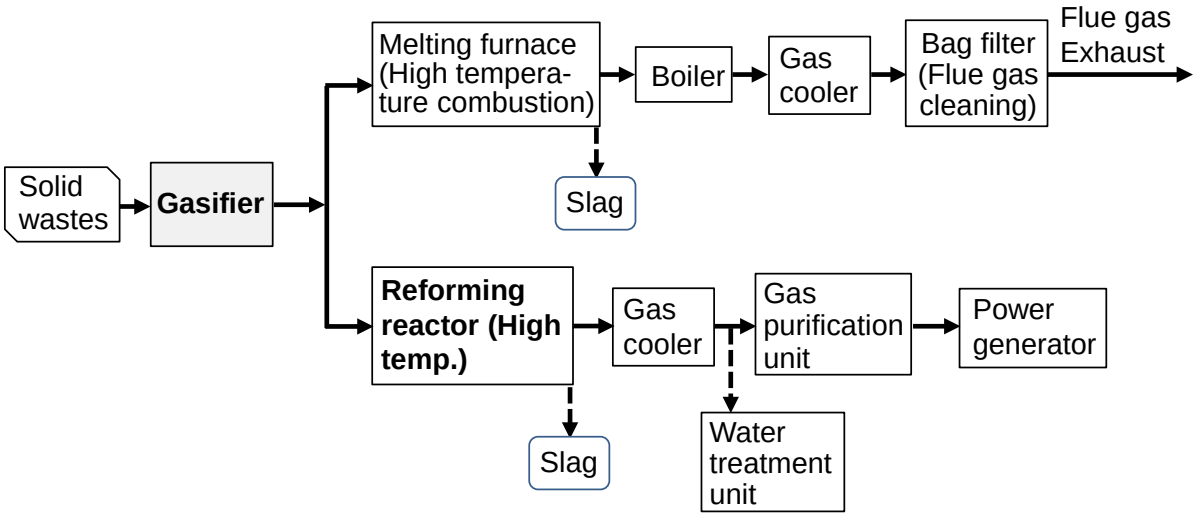

Fig. 1 Technological systems in which gasification is a major process in the thermal treatment of solid wastes

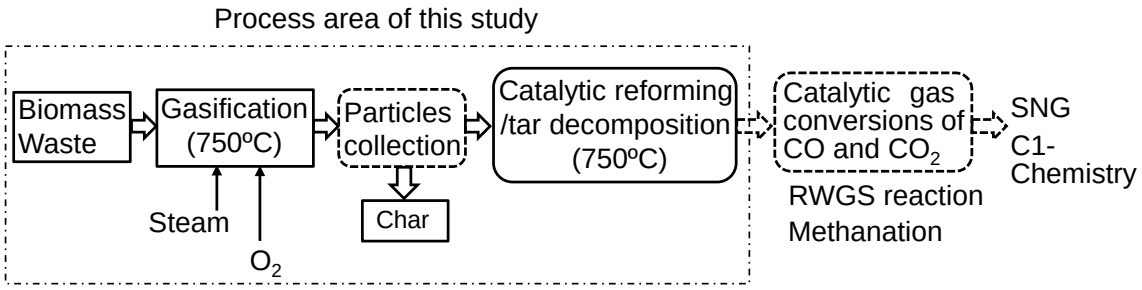

Fig. 2 Gasification and catalytic reforming process of biomass waste in this study, and possible gas conversion process design

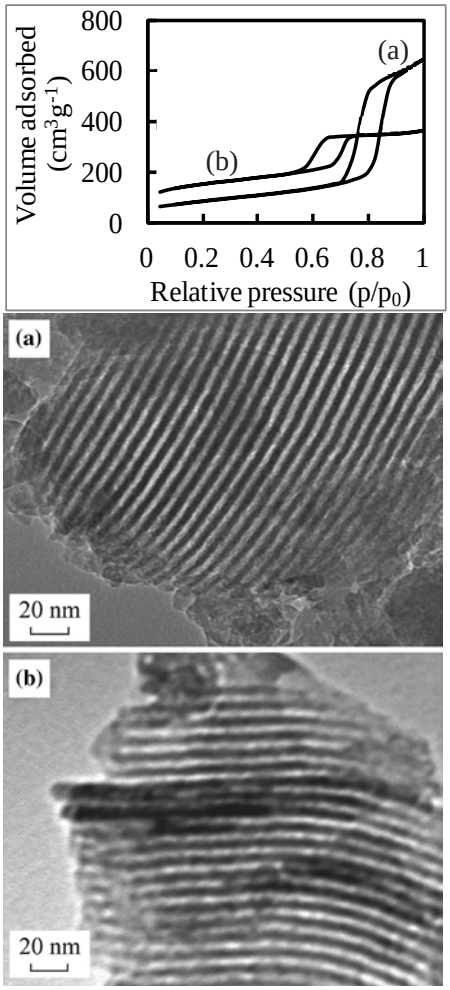

Fig. 3 Nitrogen adsorption–desorption isotherms and TEM images of 10wt%-NiO/SBA-15 obtained using the direct (a) and post-synthesis (b) methods as characterizations of meso-porous silica.

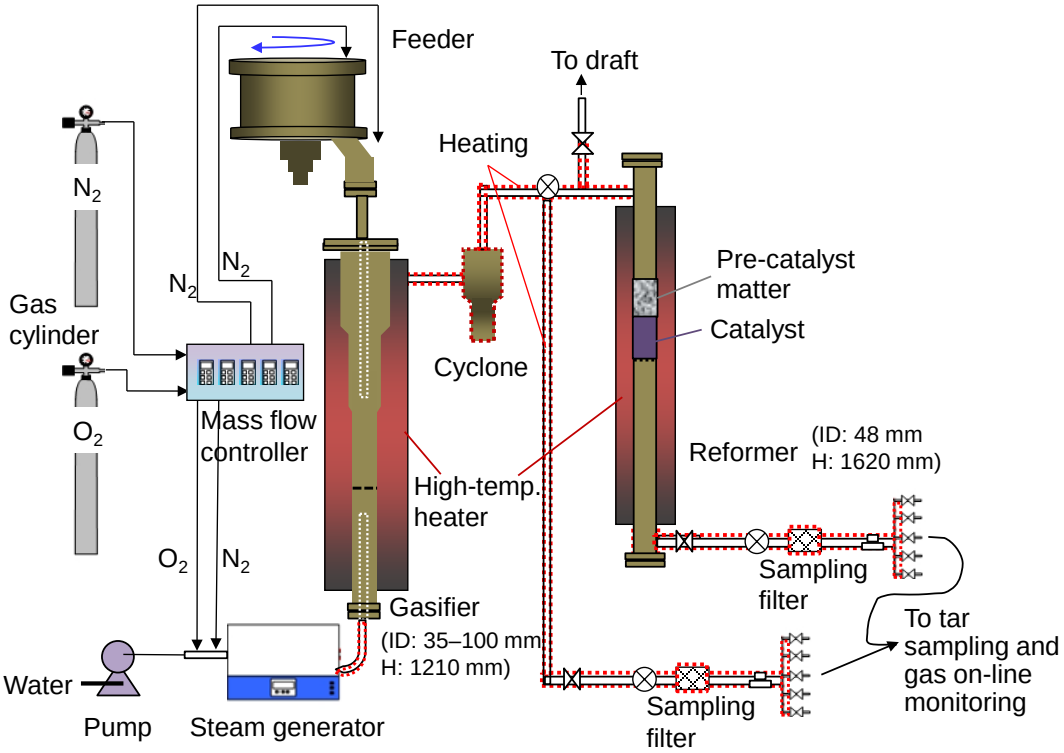

Fig. 4 Gasification and reforming experiment apparatus with gas sampling flow

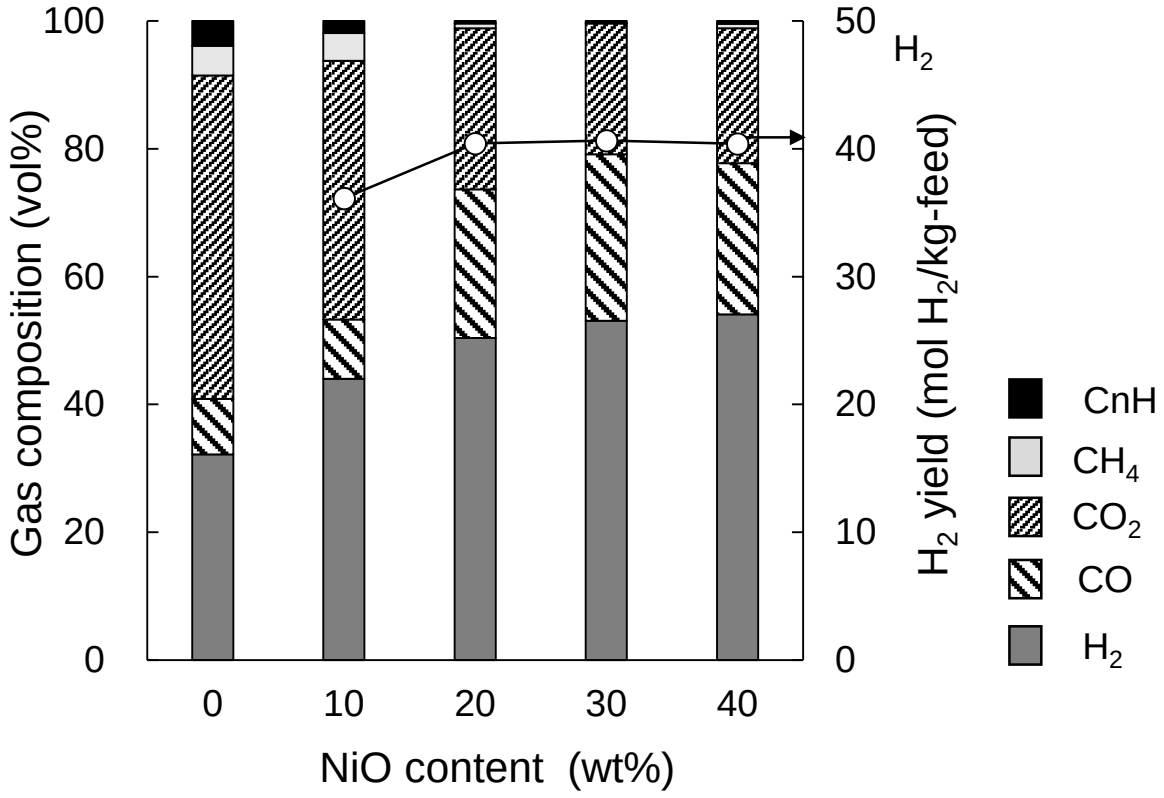

Fig. 5 Effect of NiO content on gas composition and H_2 yield in catalytic reforming
(Feedstock : Wood, Catalyst : NiO/SBA15, Temperature : 750 ^{O}C)

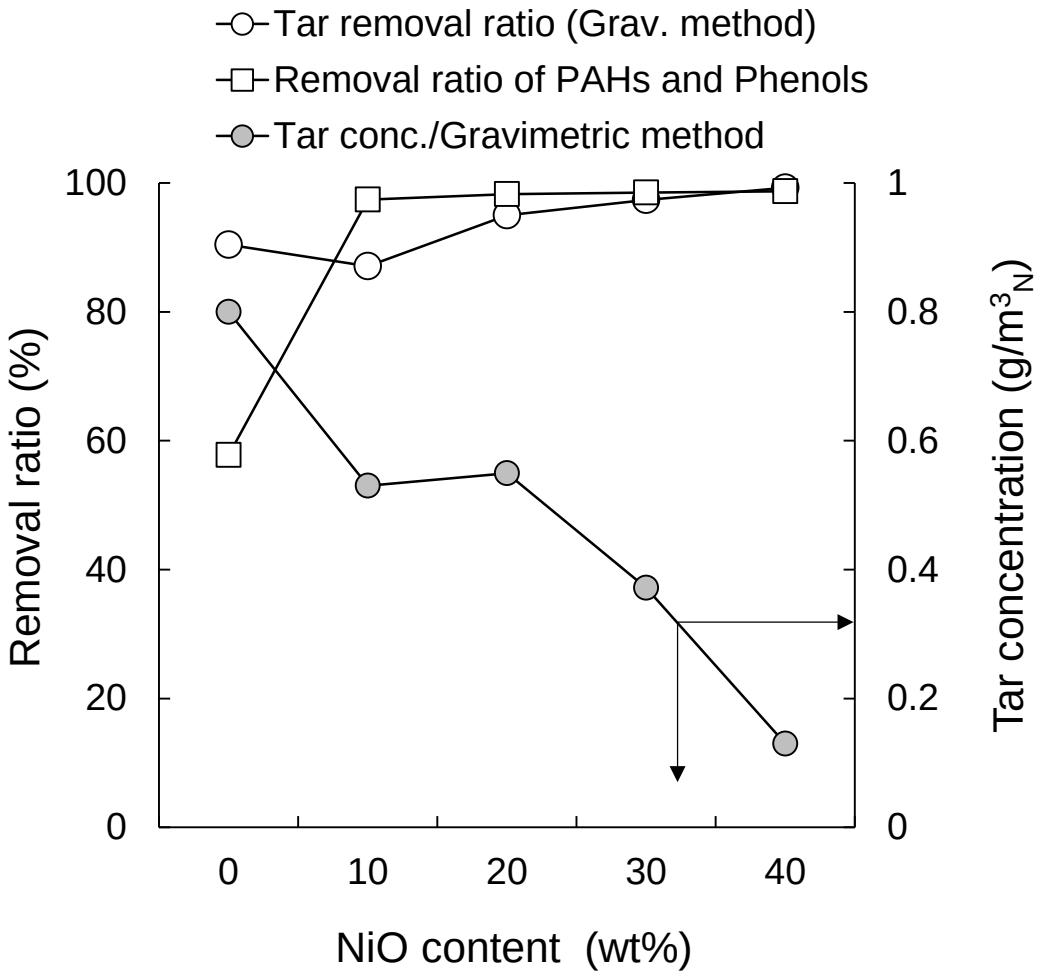

Fig. 6 Gravimetric tar, PAHs and phenols in reformed gases and removal efficiencies by NiO contents (Feedstock : Wood, Catalyst : NiO/SBA15, Temperature : 750 ºC)

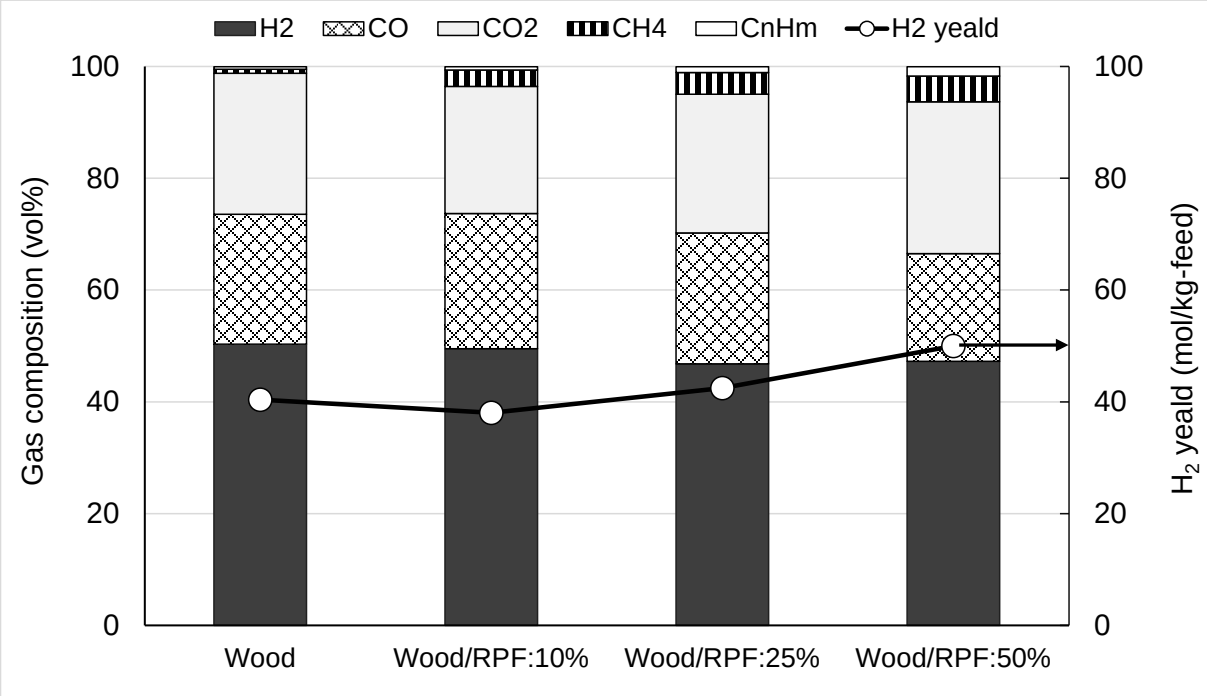

Fig.7 Gas composition and H_2 yield change with mixing RPF to wood sample
(Catalyst : 20wt%-NiO/SBA-15, Temperature : 750 ºC)